

DISTRIBUTION OF INTERNAL STATES OF CO AND OH FROM O(¹D) + C₆H₆ AND C₆D₆ DETERMINED WITH TIME-RESOLVED FOURIER-TRANSFORM SPECTROSCOPY

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Rotationally resolved infrared emission spectra of CO ($1 \leq v \leq 6$) in the spectral region 1800 – 2350 cm⁻¹ and OH ($1 \leq v \leq 3$) in the region 2800 – 3700 cm⁻¹ were recorded with a step-scan Fourier-transform spectrometer. CO shows a rotational distribution corresponding approximately to temperatures 1520 K for $v = 1$ and 860 K for $v = 2 - 6$, with an average rotational energy of 9 ± 1 kJ mol⁻¹ at the earliest applicable period (2.5 – 7.5 μ s) upon photolysis. Extrapolation to time zero based on data in the range 2.5 – 27.5 μ s yields an average nascent rotational energy of 14 ± 4 kJ mol⁻¹. Observed vibrational distribution of CO corresponds to a vibrational temperature of 5800 ± 330 K and an average vibrational energy of 33 ± 3 kJ mol⁻¹. OH shows a rotational distribution corresponding to temperatures 550 K for the P1 branch ($v = 1 - 3$) and 620 K for the P2 branch ($v = 1 - 3$), with an average nascent rotational energy of 4 ± 1 kJ mol⁻¹. The observed vibrational temperature of OH is 4830 ± 230 K, corresponding to an average vibrational energy of 21 ± 4 kJ mol⁻¹. The branching ratio of [CO]/[OH] is 2.1 ± 0.1 for O(¹D) + C₆H₆ and no OD was observed from O(¹D) + C₆D₆. The significant deuterium isotope effect will be discussed.